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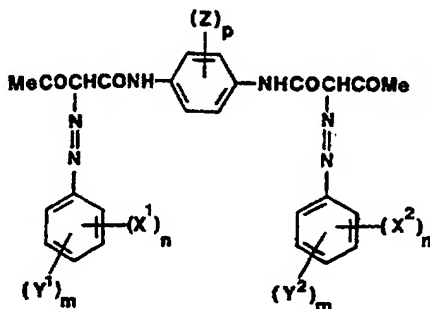
(58) Field of Search

Online: CAS ONLINE

(54) Abstract Title

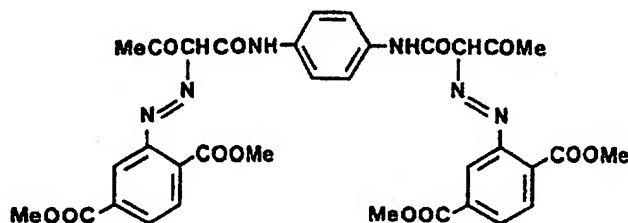
**Bis-azo compounds derived from diazotised (carboxy/sulpho)-anilines & 1,4-bis(acetoacetamido) phenylenes and their use in pigment & ink compositions**

(57) There is provided an azo compound of formula I :-



[in which the groups  $X^1$  and  $X^2$  which may be the same or different are sulphonic or carboxylic acid groups or salts thereof;  $Y^1$  and  $Y^2$  are individually a lower alkyl group, a halogen, a group OR, a group COOR (where R is a lower alkyl group) or a carboxylic acid group; Z is a sulphonic acid group or salt thereof, a carboxylic acid group or salt thereof, a lower alkyl group, a halogen, a group OR, or a group COOR (where R has the meaning defined above); m is 0, 1, or 2, n is 1 or 2, p is 0, 1, or 2; and lower alkyl group means an alkyl group comprising up to four carbon atoms].

There is also provided both a pigment composition and an aqueous ink which comprises a combination of a yellow or orange pigment and a compound of formula I. Preferably the pigment is CI Pigment Yellow 155 of formula II :-



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This invention relates to novel chemical compounds and to the use thereof for improving the dispersion properties of pigment compositions. More particularly it relates to the use for improving the dispersion properties of aqueous compositions comprising yellow or orange pigments and to the use thereof in inks.

## BACKGROUND to the INVENTION

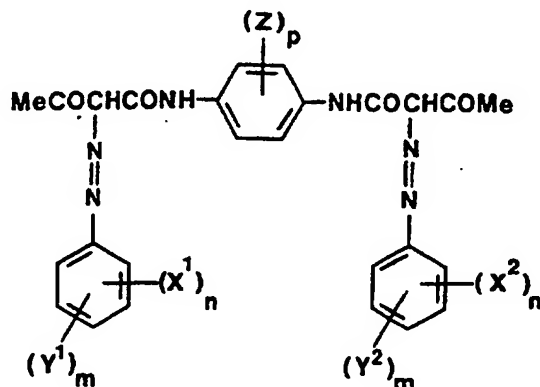
Pigments are colorants which are considered to be effectively insoluble in the application medium, and many such compounds are well known and in wide commercial use. Various classes of pigment are classified in the Pigments and Solvent Dyes section of the Colour Index International, published by the Society of Dyers and Colorists in 1997, and there are of course many other insoluble colorants which are not in this list. It is common practice to provide pigment compositions in the form of finely divided dispersions, which may be produced by well known methods such as ball milling or by the methods disclosed in United States Patents 5026427 and 5310778. In order to obtain the optimum dispersion properties it is common to have present at least one dispersant or surfactant, and it is well known that the choice of dispersant is very important for achieving these properties. The purpose of the dispersant is to stabilise the particles and to prevent growth by aggregation or flocculation. The dispersant or dispersants may be incorporated into the pigment at synthesis or during an aftertreatment, may be added before or during the dispersion stage, may be added to the final dispersion or formulation, or may be added in a combination of these ways. Suitable dispersants are well known, and include, for example, polymers such as styrene/acrylic acid and styrene/maleic acid resins, surfactants such as alkyl phenol ethoxylates, and coloured compounds such as dyes which are structurally related to the pigment in use. For instance

United States Patent 2816045 discloses the use of salts of copper phthalocyanine sulphonic acids to improve the flocculation resistance of formulations comprising copper phthalocyanine pigments, United States Patent 3386843 discloses salts of sulphonated quinacridone compounds and their use for improving the tinctorial and rheological properties of compositions comprising structurally related quinacridone pigments, and European Patent Application 451094 and Japanese Patent Application 63 178169 disclose sulphonated diarylide azo compounds and the use thereof in combination with related benzidine type yellow pigments.

We have discovered a new class of yellow disazo dye which is useful for improving the properties of dispersions comprising certain high performance disazo pigments such as those disclosed in German Patentschriften 1150165 and 1544453, British Patent Applications 1348714 and 1342140, and United States Patent specifications 3997521, 4003886, and 4070353. This class of pigment has excellent performance properties, but it can be difficult to achieve an adequately fine particle size from dispersions comprising such pigments without problems of aggregation or flocculation, and formulations may be subject to settling out.

#### SUMMARY of the INVENTION

According to the present invention there is provided a compound of general structure I:-



In which the groups  $X^1$  and  $X^2$  which may be the same or different are sulphonic or carboxylic acid groups or salts thereof,  $Y^1$  and  $Y^2$  are individually a carboxylic acid group, a lower alkyl group, a halogen, a group OR, or a group COOR where R is a lower alkyl group, Z is a sulphonic acid group or salt thereof, a carboxylic acid group or salt thereof, a lower alkyl group, a halogen, a group OR, or a group COOR where R has the meaning defined above, m is 0, 1, or 2, n is 1 or 2, and p is 0, 1, or 2. By lower alkyl group is meant an alkyl group comprising up to four carbon atoms. Preferably the lower alkyl group is ethyl or methyl, and most preferably it is methyl. Preferably the groups  $X^1$  and  $X^2$  are the same and the groups  $Y^1$  and  $Y^2$  are the same. Preferably p is 0. When the groups  $X^1$  and  $X^2$  are salts of carboxylic or sulphonic acids then the counterions may individually be an alkali metal cation such as lithium, sodium, or potassium, an alkaline earth or other metallic cation, an ammonium cation, or a substituted ammonium cation such as triethanolammonium, triethylammonium, or pyridinium.

Specific useful compounds of formula I include the following:

COMPOUND	$(X^1)_n$	$(X^2)_n$	$(Y^1)_m$	$(Y^2)_m$	$Z_p$
A	4-SO <sub>3</sub> Na	4-SO <sub>3</sub> Na	H	H	H
B	2,5-(COONa) <sub>2</sub>	2,5-(COONa) <sub>2</sub>	H	H	H
C	3-SO <sub>3</sub> Na	3-SO <sub>3</sub> Na	H	H	H
D	2-SO <sub>3</sub> Na	2-SO <sub>3</sub> Na	H	H	H

Compounds of Formula I may be prepared by well known methods, and in particular by the standard synthetic method for azo dyes wherein a suitable amine is diazotised and coupled with the appropriate acetoacetamide. The *bis*-acetoacetamides required for the preparation of the compounds of formula I by this reaction are known compounds according, for example, to United States Patents 4254025 and 4234480 or may be prepared by known methods such

as those described in USP 4254025. In the case that the groups  $X^1$  and  $X^2$  or  $Y^1$  and  $Y^2$  are different then the compounds may be prepared by a suitable mixed diazotisation as is known in the art as, for example, described in USP 4234480, but will be formed in admixture with the corresponding symmetrical compounds. It is to be understood that the compounds of formula I are written in the conventional azo tautomeric structure, but may exist partly or completely in alternative keto-hydrazone or other tautomers as is known for certain azo compounds. The formula I hence also embraces these other tautomeric structures.

#### DETAILED DESCRIPTION of the INVENTION

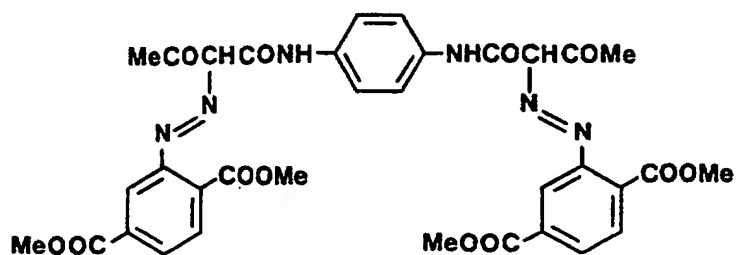
The compounds of the invention are useful for improving the dispersion properties of pigment compositions comprising certain yellow and orange disazo pigments such as those disclosed by German Patentschriften 1150165, 1544453, British Patent Applications 1348714 and 1342140, and United States Patent specifications 3997521, 4003886, and 4070353, together with the mixed pigments disclosed in United States Patent specification 5030247. They are particularly useful for improving the dispersion properties of the disazo pigments of United States Patents 3997521 and 4003886.

Therefore according to a second aspect of the invention there is provided a pigment preparation which comprises a combination of a yellow or orange pigment and a compound of formula I. The proportion of compound of formula I in the mixture may be up to 100% by weight on the pigment, but is preferably between about 1% and about 25%, and most preferably between about 1% and about 10% by weight on the pigment. According to this aspect the solubilising groups  $X^1$  and  $X^2$  of the compound of formula I are preferably in the

salt form. According to convenience the compound of formula I may either be synthesised in the salt form or it may be prepared in the form of the free acid and neutralised for use by addition of a suitable base. Suitable bases include ammonia, organic amines, basic salts of metallic cations, and mixtures of such bases. Preferably the base is an alkali metal hydroxide.

The compound of formula I may be added to the pigment at synthesis, as disclosed for example in United States Patent 5151129, as a treatment after the synthesis, or alternatively the compound of formula I and the pigment may be co-synthesised by a suitable mixed coupling reaction as is known in the art.

It is particularly preferred according to this aspect of the invention that the pigment is the compound shown as formula 20 of USP 3997521 and formula 2 of USP 4003886. This pigment is catalogued as Pigment Yellow 155 by the Colour Index and has the structure II below.



It is to be understood that the structure for the compound of formula II is shown as the conventional azo tautomer, but that the pigment may exist in the alternative keto-hydrazone form as is generally the case for yellow azo pigments (see for example the article by K.Hunger in Review of Progress in Coloration, volume 29, 1999 page 74).

It is common practice to provide pigment compositions in the form of finely divided dispersions in a suitable carrier or solvent, which may be produced by a dispersion stage subsequent to the synthesis of the pigment. According to a third aspect of the invention there is provided a pigment dispersion which comprises a combination of a yellow or orange pigment and a compound of formula I dispersed in an aqueous solvent. By aqueous solvent is meant a solvent wherein the liquid phase is predominantly water, but which may also comprise in addition at least one water soluble organic cosolvent. The proportion of compound of formula I may be up to 100% by weight on the pigment, but is preferably between about 1% and about 25%, and most preferably between about 1% and about 10% by weight on the pigment. According to this aspect the solubilising groups  $X^1$  and  $X^2$  of the compound of formula I are preferably in the salt form.

According to this aspect it is preferred that the compound of formula I be added to the pigment at the dispersion stage. There may also be present in the dispersion at least one additional dispersant or surfactant. This additional dispersant or surfactant may be added to the pigment at synthesis, may be added as a grinding aid at the dispersion stage, or may be added after the dispersion stage. Suitable additional dispersants may include any of the dispersant types known in the art, but preferably the additional dispersant is a nonionic dispersant. There may also be present in the dispersion other additives or cosolvents.

A suitable concentration for the pigment in a dispersion is up to about 50% depending on the dispersing method and the end use. A concentration of about 20 to about 25% is most suitable. If an additional dispersant is used then this may be present at up to 100% by weight on the pigment, but is preferably present at up to about 50% by weight on pigment.

According to this aspect it is particularly preferred that the pigment in the dispersion is the yellow pigment of formula II.

According to another aspect of the invention there is provided an aqueous ink which comprises a combination of a yellow or orange pigment and a compound of formula I.

According to this aspect the solubilising groups  $X^1$  and  $X^2$  of the compound of formula I are preferably in the salt form. By aqueous ink is meant an ink wherein the liquid phase is predominantly water, but which may also comprise at least one additional water soluble organic cosolvent. The ink compositions of the invention may also contain other components which are advantageously added to aqueous inks, such as surfactants, viscosity modifiers, biocides, and metal sequestering agents. Such additional components are well known in the art.

According to this aspect it is particularly preferred that the pigment in the ink is the yellow pigment of formula II. Therefore according to this aspect there is provided an ink which comprises a combination of the pigment of formula II with the compound of formula I. The proportion of compound of formula I may be up to 100% by weight on the pigment, but is preferably between about 1% and about 25%, and most preferably between about 1% and about 10% by weight on the pigment.

The aqueous ink compositions of the invention are especially suited to use in ink jet printers. According to this aspect it is preferred that there is at least one organic cosolvent present in the ink, and most preferred that there is a combination of cosolvents present in the ink.



Suitable cosolvents are well known in the art, and include lower aliphatic alcohols and ketones, glycols, polyhydric alcohols, poly(ethylene oxides), glycol ethers, heterocycles such as dioxan or tetrahydrofuran, nitrogen containing compounds such as urea, pyrrolidone, and alkyl pyrrolidones, and sulphur containing compounds such as sulpholane and thiodiglycol.

For this use, the concentration of the pigment composition in the ink is preferably between about 1% and about 8% and the concentration of organic cosolvents in the ink is preferably between about 10% and about 50%, and most preferably between about 15% and about 25%. It is preferred to prepare inks by dispersing the pigment in the presence of the compound of formula 1 in deionised water to provide a dispersion, and then to dilute this dispersion to form the ink by adding additional water together with the organic cosolvents and any other additives.

United States Patents 4254025 discloses certain azo dyes according to the general structure I wherein the groups Y<sup>1</sup> and Y<sup>2</sup> are styryl groups. Similarly United States Patent 4234480 discloses certain azo dyes according to the general structure I wherein the groups Y<sup>1</sup> and Y<sup>2</sup> are benzothiazole or naphthotriazole substituents. However these dyes are provided as direct dyes for cellulosic substrates and not for use in pigment compositions.

The following examples will serve to illustrate the invention.

## EXAMPLES

### Synthesis Example 1 - preparation of compound A

Nitrosyl sulphuric acid (1.92g; 15 mmol) was added portionwise to a stirred, chilled mixture of sulphanilic acid sodium salt (1.94g; 10 mmol) in water (20 ml) and concentrated hydrochloric acid (2.4 ml) so as to keep the internal temperature below 5°. The mixture was stirred in ice for a further 15 min and then was added dropwise during *ca* 10 min to a briskly stirred, chilled solution of *bis* acetoaceto-1,4-phenylenediamide (1.38g; 5 mmol), sodium hydroxide (1.6g; 40 mmol) and anhydrous sodium acetate (1.4g; 17 mmol) in water (40 ml). A red-orange colour developed initially after which a yellow solid was precipitated. The mixture was stirred for 1h at room temperature, then for 15 min at 95-100° (oil bath temperature). The mixture was allowed to cool overnight, filtered, and washed (water; methanol). The crude material was then heated under reflux in methanol (40 ml) for 2h, filtered, washed (methanol; ether) and dried *in vacuo* over phosphorus pentoxide to afford compound A as a yellow solid 3.05g. (88%).

Mp > 360°.  $\lambda_{\text{max}}$  (H<sub>2</sub>O) = 375 nm.

C<sub>26</sub>H<sub>22</sub>N<sub>6</sub>NaO<sub>10</sub>S<sub>2</sub> Requires: C = 45.4%, H = 3.3%, N = 12.2%. Found: C = 45.7%, H = 3.8%, N = 12.4%.

### Synthesis Example 2 - preparation of compound B

Nitrosyl sulphuric acid (1.53g; 11.95 mmol) was added portionwise to a stirred, chilled mixture of 2-aminoterephthalic acid (1.81g; 10 mmol) in glacial acetic acid (30 ml), concentrated hydrochloric acid (13 ml), water (6 ml) and 2-methoxyethanol (25 ml) whilst maintaining the internal temperature below 5°. The mixture was stirred in an ice-bath for a

further 1h. This solution was then added during ca 10 min to a rapidly stirred, chilled solution of bis acetoacet-1,4-phenylenediamide (1.32g; 4.8 mmol), sodium hydroxide (16g) and sodium acetate (16g) in water (275 ml). Towards the end of the addition a yellow solid was deposited from the orange solution. The mixture was stirred for 1h, heated at 90-100° (oil bath temperature) for 1h and then cooled in an ice-bath. The solid was filtered, washed (water; methanol; acetone) and dried. This crude material was heated at reflux in methanol (60 ml) for 4½h, allowed to cool to room temperature, filtered and dried *in vacuo* over phosphorus pentoxide to furnish compound **B** as an ochre-brown solid 2.70g. (73%).

Mp >360°,  $\lambda_{\text{max}}$  = 370 nm.

$\text{C}_{30}\text{H}_{20}\text{N}_6\text{Na}_4\text{O}_{12}\cdot\text{H}_2\text{O}$  Requires: C = 47.0%, H = 2.9%, N = 11.0%. Found: C = 46.8%, H = 3.4%, N = 11.5%.

The following additional compounds were prepared similarly:-

Compound	Melting point
<b>C</b>	325-327°(dec)
<b>D</b>	>360°

## Testing Example 1

Preparation of Dispersion

Compound A (0.1g) was dissolved in water (90g) using a magnetic stirrer, and a commercial sample of Pigment Yellow 155 (10g) (available under the trade name Novoperm<sup>(RTM)</sup> Yellow 4G) was added while stirring. Once this had wetted out the composition was transferred to a Silverson mixer and mixed for 10minutes while the dispersing properties were observed.

After a further 10minutes mixing the composition was transferred to a M110-F Microfluidiser and dispersed for 10minutes at 13000psi. Oversized particles were then removed by centrifugation at 3000rpm for 20 minutes to provide the final dispersion. This is dispersion 1 and it was compared with an inventive dispersion 2 prepared using a greater quantity of compound A, with a comparative dispersion prepared using the commercially available dispersant Sodium N-lauroyl sarcosinate, and with two control dispersions prepared as follows:-

DISPERSION	Addition	Observation
1 above (invention)	0.1g Compound A	Wetted and dispersed well
2 (invention)	0.3g Compound A	Wetted and dispersed well
3 (comparison)	1g Sodium Lauroyl Sarcosinate	Wetted and dispersed well
4 (control)	Potassium p-Toluene Sulphonate	Thickened uncontrollably
5 (control)	None	Did not wet or disperse

Inks were prepared from these dispersions by taking 17.5g of the dispersion and letting down to 50g by adding a mixture comprising by weight urea (5%), thiodiglycol (10%), polyethylene glycol 300 (10%), and water (75%). The average particle size of the dispersions and of the inks was determined using a Polymer Laboratories Light Scattering Photometer.

The results are given below:-

Reference	Particle size of dispersion	Particle size of ink
1 (invention)	174nm	172nm
2 (invention)	168nm	171nm
3 (comparison)	177nm	184nm

It is seen that a marginally smaller measured particle size was achieved with the dispersions prepared using the inventive compound A despite this compound being used in smaller quantity than the commercial dispersant in the comparison dispersion. Moreover the inventive dispersions could be formulated into inks without any significant change in the measured particle size, showing that they are robust to the shock of changing the solvent at let down, whereas the comparison dispersion showed a slight increase in the measured particle size, though this is probably not significant.

### Stability

The stability of the dispersions and inks was assessed by taking 5g samples in small sealed plastic tubes and storing in a water bath at 70° for four weeks. They were regularly inspected for evidence of instability such as flocculation or settling. None of the dispersions or inks showed any sign of settling out during this period, and both were judged to show excellent stability.

Samples of the inks were stored at room temperature for one month, care being taken not to allow any agitation. The samples were inspected weekly for any evidence of settling out. At the end of four weeks there was some slight settling of the comparison ink 3, but no evidence of any settling in the inks 1 and 2 prepared using compound A. The inventive ink thus shows excellent storage stability, better than that of the control.

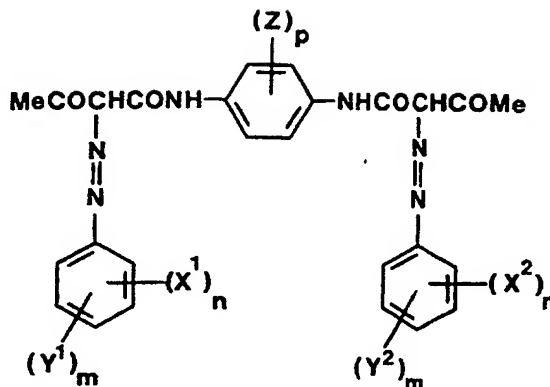
#### Printing Performance

An HP51626a ink jet printer cartridge was filled with the inventive ink 2 and placed in an HP400 desk top ink jet printer. A solid fill test pattern was then printed. The ink printed successfully and gave a print having a uniform fill of colour with good density showing that the inventive ink has excellent printing performance.

The decap performance of the ink was evaluated by leaving the filled ink cartridge uncapped for periods of 1 day and 4 days, and then printing another test pattern. The cartridge fired up immediately on both occasions showing that the inventive ink has excellent decap performance.

Claims

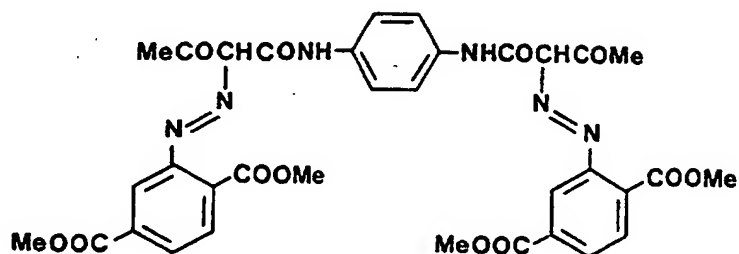
1. A compound of general formula I



In which the groups  $X^1$  and  $X^2$  which may be the same or different are sulphonic or carboxylic acid groups or salts thereof,  $Y^1$  and  $Y^2$  are individually a carboxylic acid group, a lower alkyl group having up to four carbon atoms, a halogen, a group OR, or a group COOR where R is a lower alkyl group as defined above, Z is a sulphonic acid group or salt thereof, a carboxylic acid group or salt thereof, a lower alkyl group as defined above, a halogen, a group OR, or a group COOR where R has the meaning defined above, m is 0, 1, or 2, n is 1 or 2, and p is 0, 1, or 2.

2. A compound of formula I according to claim 1 wherein the groups  $X^1$  and  $X^2$  are the same and wherein m is 0 and p is 0.
3. The compounds of structure A, B, C, or D as shown herein.
4. A pigment preparation which comprises a combination of at least one yellow or orange pigment and at least one compound of formula I.

5. A pigment preparation according to claim 4 wherein the yellow pigment is the compound of formula II.



6. An aqueous ink which comprises a combination of a yellow or orange pigment and at least one compound of formula I.
7. An ink according to claim 6 wherein the yellow pigment is the compound of formula II.





Application No: GB 9928109.9  
Claims searched: 1-7

Examiner: Stephen Quick  
Date of search: 17 April 2000

**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.R):

Int Cl (Ed.7):

Other: Online: CAS ONLINE

**Documents considered to be relevant:**

Category	Identity of document and relevant passage	Relevant to claims
X	GB 1497437 A (CHEMETRON) and Chemical Abstracts, abstr no 84:6482, see compound RN 57532-26-0	1 at least
X	GB 1453345 A (CIBA-GEIGY) and Chemical Abstracts, abstr no 83:29846, see compound RN 55489-24-2	1 at least
X	US 5559216 A (HOECHST) and Chemical Abstracts, abstr no 121:111471, see compound RN 156564-68-0	1 at least
X	Chemical Abstracts, abstr no 116:237351 & CS 266083 B1, see abstract and compounds RN 57440-77-4, 60728-43-0 & 74351-78-3	1 at least
X	Chemical Abstracts, abstr no 107:238569 & CS 219960 B, see abstract and compounds RN 60728-42-9, 74351-78-3 & 94470-53-8	1 at least
X	Chemical Abstracts, abstr no 101:132460 & CS 208620 B, see abstract and compounds RN 60728-42-9, 74351-78-3, 91991-61-6 & 91991-64-9	1 at least
X	Chemical Abstracts, abstr no 100:105186 & JP 580101161 A2 16.06.1983, see abstract and compound RN 89190-21-6	1 at least
X	Chemical Abstracts, abstr no 93:73763 & CS 181528 B, see abstract and compounds RN 74351-78-3, 74351-80-7, 74351-81-8, 74351-84-1 & 74351-92-1	1 at least

X Document indicating lack of novelty or inventive step  
Y Document indicating lack of inventive step if combined with one or more other documents of same category.

& Member of the same patent family

A Document indicating technological background and/or state of the art.  
P Document published on or after the declared priority date but before the filing date of this invention.  
E Patent document published on or after, but with priority date earlier than, the filing date of this application.



Application No: GB 9928109.9  
Claims searched: 1-7

Examiner: Stephen Quick  
Date of search: 17 April 2000

Category	Identity of document and relevant passage	Relevant to claims
X	Chemical Abstracts, abstr no 83:165805 & JP 500011411 B4 01.05.1975, see abstract and compound RN 56725-82-7	1 at least

N	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.